

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

This Page Blank (uspto)



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A01N 25/34, 25/04, B65D 65/38		A1	(11) International Publication Number: WO 92/01378 (43) International Publication Date: 6 February 1992 (06.02.92)
(21) International Application Number: PCT/EP91/01352 (22) International Filing Date: 18 July 1991 (18.07.91)		(74) Agents: BENTHAM, Stephen et al.; J.A. Kemp & Co., 14 South Square, Gray's Inn, London WC1R 5LX (GB).	
(30) Priority data: 554,615 18 July 1990 (18.07.90) US 680,590 4 April 1991 (04.04.91) US		(81) Designated States: AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC, MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, SD, SE, SE (European patent), SN + (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent).	
(71) Applicant: RHONE-POULENC AGROCHIMIE [FR/FR]; 14-20, rue Pierre-Baizet, F-69009 Lyon (FR).		Published <i>With international search report.</i>	
(72) Inventors: CHEN, Chi-Yu, R. ; 10004 Whitestone Road, Raleigh, NC 27615 (US). GOUGE, Samuel, T. ; 1708 Parkridge Way, Raleigh, NC 27614 (US). HODAKOWSKI, Leonard, E. ; 8205 S Crestwyck Court, Raleigh, NC 27615 (US). WEBER, Paul, J. ; 3515-A Century Oaks Road, Durham, NC 27713 (US).			
(54) Title: GEL FORMULATIONS FOR USE IN TOXIC OR HAZARDOUS PRODUCT CONTAINERISATION SYSTEMS			
(57) Abstract			
A water dispersible organic gel which is a continuous system comprising: a hazardous product, a water soluble or water dispersible surfactant, a gelling agent and a plasticising agent. The gel is useful in a containerisation system, e.g. in a water soluble or dispersible bag and renders the hazardous product safer to handle and for the environment.			

+ DESIGNATIONS OF "SU"

It is not yet known for which States of the former Soviet Union any designation of the Soviet Union has effect.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU+	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

- 1 -

GEL FORMULATIONS FOR USE IN TOXIC OR HAZARDOUS
PRODUCT CONTAINERISATION SYSTEMS

The invention relates to new water dispersible organic gels and containerisation systems containing them.

5 These containerisation systems are suitable for containing hazardous products to render them safer to handle and for the environment.

At present, most hazardous liquids are stored in metal drums or, where smaller quantities are required,

10 plastic containers.

Hazardous compounds, especially agrochemical compounds are formulated in various compositions. Liquid composition are most convenient for farmers because of the relative ease with which they can be handled. There are,

15 nevertheless, difficulties in handling such liquid compositions. There is a danger of spillage or leakage if there are holes in the containers previously used or if they are dropped. Although secure containers resistant to shock can be used, in the event of an accident, for example during

20 transportation, the risk remains of spillage or leakage with rapid loss of liquid, for example leaking onto the ground.

It has been difficult to provide a formulation and a containerisation system (i.e. container) which safeguards those handling it, including farmers and transporters, and

25 the environment.

- 2 -

It is known to have agrochemicals in soluble bags or sachets, but that does not avoid completely the possibility of the bag cracking and breaking and the liquid creating a contamination problem. More specifically, when water soluble bags are used, the agrochemical compositions contained in the bag are organic ones, that is to say nonaqueous solvent-based compositions and, more or less, the solvent has the tendency to extract the adjuvant and additives of the film and to render the wall (film) of the bag more brittle (especially at low temperature and more specifically at temperature below 0°C) or to reduce its service life.

It was known to use gel formulations for pharmaceuticals or cosmetics, but there is practically no risk of pollution or contamination of environment when handling such products, in contrast to pesticides and agrochemicals. Furthermore the gels used for pharmaceutical or cosmetical purposes are generally water-based, so that it was unobvious to obtain gels, which are convenient for water soluble sachets or bags, nor for agrochemicals containing water soluble sachets or bags, nor for shock absorption purposes for such bags.

Furthermore, and in a practical point of view, higher concentrations of active ingredient may be obtainable when using gels instead of liquids.

The present invention seeks to provide new formulations and a new formulation system containing agrochemicals which are safe for everybody, specially the farmer and those who handle the agrochemicals.

- 3 -

The invention also seeks to provide new formulation system for agrochemicals which is easy to put in a containing system and which is easy to manipulate by the farmer.

The invention also seeks to provide new formulations and a new formulations system for agrochemicals which are readily soluble and/or dispersible in water. This is a problem which is especially difficult to overcome because the increase in viscosity is often connected with an increased difficulty to disperse in water.

The invention also seeks to provide a new formulation system for agrochemicals which is as condensed as possible, using the least amount of space.

The invention also seeks to provide new formulations and a new formulation system to contain hazardous compounds, e.g., agrochemicals which reduce the risk of contamination.

The invention also seeks to provide new formulations and a new formulation system to contain smelling or stinking compounds, e.g., agrochemicals which remove the odors or reduce odor problems.

The invention also seeks to avoid breakage of the container that contains an agrochemical formulation. When the container is brittle and rigid, there is a distinct possibility of simple breakage, but the liquid still transmits the shocks and there is the problem of hydraulic hammer effect. The invention seeks to avoid, or at least partially reduce, this hydraulic hammer effect. The invention also seeks to provide a formulation or composition for hazardous compounds that dissipate, as much as possible, the energy of an external shock to a container.

SUBSTITUTE SHEET

- 4 -

The invention also seeks to provide a shock absorbing formulation system for containing agrochemicals, e.g., pesticides or plant protection agents or plant protection agents or plant growth regulators.

The invention also seeks to provide a formulation which further extends the service life of the water soluble bag or sachet during storage, such as preventing the bag film from becoming brittle at freezing temperature.

The invention further seeks to provide a new formulation system for agrochemicals which quickly dissolves when put into water and which is not damaged by normal freezing.

The invention further seeks to provide a new formulation system for agrochemicals which reduces the risks of clogging the spray nozzles or the filters of spray tanks.

The present invention provides a water dispersible organic gel which is a continuous system comprising:

a hazardous product, as active ingredient, e.g. an agrochemical (especially a pesticide, a plant protection agent, a plant growth regulator or plant nutrient);
optionally organic solvent;
a water soluble or water dispersible surfactant;
a gelling agent; and
a plasticising agent.

The gels are especially suitable to be contained in a water soluble or water dispersible bag.

The gelling agent or thickener is a compound that substantially increases the viscosity of an organic solution.

The gelling agent which is used in the present invention may be liquid or preferably solid. The gelling agent is preferably soluble at a concentration of at least

- 5 -

10% by weight in a liquid mixture of the hazardous product, surfactant and organic solvent, if present, at a temperature above 50°C. If solid, it generally has a particle size of less than 100 microns, preferably less than 40 microns, more 5 preferably less than 20 microns and most preferably less than 10 microns.

Preferred gelling agents include tetramethyl decyne diol, ethoxylated dialkylphenol, methylated clay, propylene carbonate, hydrogenated castor oil, ethoxylated vegetable 10 oil, diatomaceous earth, mixtures of dioctyl sodium sulfosuccinate and sodium benzoate, mixtures of hexanediol and hexynediol, and a polyacrylic acid polymer or copolymer, optionally in the form of a salt and optionally crosslinked (e.g. partially crosslinked).

15 By the word surfactant, it is meant an organic material which substantially reduces the surface tension of water.

Surfactants which are particularly suitable for the invention are defined by the following test: according to 20 this test, the liquid active ingredient in organic solvent, if present in the gel, (50g in total) and surface-active adjuvant (5g) are added to an amount of water, at 50°C, which is sufficient to bring the volume of the mixture to 100ml; the mixture is agitated so as to give a homogeneous 25 emulsion and this is left to stand for 30 mintues at 50°C in a graduated cylinder; the amount of oily layer which may have separated out (and thus formed a distinct liquid phase) must then be less than 20 ml.

The surfactant that is used in the invention may be 30 nonionic, anionic or actionic, or may be zwitterionic.

Amphoteric surfactants may be used. A mixture of surfactants may also be used. Preferably the surfactant is able to form a liquid mixture, preferably a liquid phase, with hazardous product and organic solvent, if present, at a 35 temperature above 70°C, preferably above 50°C. This liquid

- 6 -

mixture may be in the form of a single continuous phase or of an emulsion. Another preferable feature of the surfactant is that it contains at least 10% of a surfactant having hydroxy and/or alcoxy groups, such as polyethoxylated 5 or polypropoxylated derivatives. Especially preferred are derivatives of fatty amine or fatty acids or fatty alcohols or aryl phenols.

Preferred surfactants include nonionic surfactants,

10 optionally mixed with an ionic surfactant, and which are able to form a liquid mixture with the hazardous product and organic solvent, if present, at a temperature above 50°C, preferably above 70°C.

The hereinbefore defined gel may optionally contain 15 the further following components:

an organic or mixture of organic solvents in which therein the hazardous product is soluble e.g. completely soluble at room temperature;

a dispersant;

20 a secondary thickener;

such as a polyacrylic acid polymer, optionally in the form of a salt or a copolymer and optionally cross-linked (eg. partially cross-linked); fumed silica; hydroxyethyl cellulose carboxy-methylcellulose; organically modified 25 attapulgite or montmorillonite clay; hardened castor oil; cetyl and stearyl alcohols or esters; polyethylene glycols; glycerol hydroxystearate, polyvinylalcohol (of low molecular weight), dioctyl sodium sulfosuccinate and sodium benzoate; alkyl benzene sulfonates; xantham gum, polyvinylpyrrolidone; 30 or polyvinyl acetate;

other additives such as antifoam agents, stabilizers, buffers and antifreezing agents.

Among the gels of the invention as hereabove defined, some particular gels are preferred, especially 35 those comprising by weight:

5 to 95%, preferably 10 to 90%, more preferably 25 to 80%, of hazardous product;

-7-

1 to 50%, more preferably 2 to 20%, of surfactant;
0.1 to 50%, preferably 0.5 to 10% of gelling agent;
0 to 80%, preferably 3 to 50%, of solvent;
0 to 20% preferably 0.1 to 10% of plasticising agent;
optionally 0.1 to 20%, preferably 2 to 8%, of a dispersant;
and
0 to 20%, preferably 0.1 to 10%, of other additives,

The plasticising agent which may be used in the invention is preferably a compound that is able to reduce the glass transition temperature of polyvinyl alcohol to below room temperature.

Furthermore this plasticising agent is preferably compound that is water soluble or water dispersible and is soluble at a concentration of at least 0.1% by weight in a liquid mixture of the hazardous product, the surfactant and optionally organic solvent, if present.

The plasticising agent, for example selected from:

alcohols compounds (linear or branched, saturated or unsaturated), especially alcenols having from 6 to 36 carbon atoms; alcenols having from 10 to 30 carbon atoms; glycols and triols such as di- and tri-. pentaerythritol, trimethylethane, anhydroenneaheptitol, butanetriol, hexanetriol, erythritols, threitol, ribitol, arabinitols, xylitol, allitol, dulcitol, glucitol, sorbitol mannitol, altritol, iditol, maltitol, lactitol, ethyleneglycol, diethyleneglycol, triethyleneglycol, trimethyleneglycol, tetramethyleneglycol, pentamethyleneglycol, hexamethyleneglycol, propyleneglycol, glycerol, 2,3-butanediol, 1,3-butanediol, mono-, di-, tri-, tetra-, and poly-amines, such as diethylenetriamine and ethanolamines; amides, e.g., acetamide and formamide,

-8-

dimethylformamide, hexamethylphosphotriamide; sulfoxides, e.g., dimethylsulfoxide; piperazines.

The plasticising agents (or bag softener) that may be used in invention as described above impart and maintain softness to a container such as a bag containing the gel. They thus help to prevent the container from breaking during handling or storage,

especially at low freezing temperatures (e.g., under -20°C).

Thus there is little chance for contamination or pollution to occur under these severe conditions.

According to a particular feature of the invention, the components of the compositions of the invention are chosen in such a way that one or more of the following feature are present:

* the resulting gels have a viscosity of 500 to 30,000 centipoise, more preferably of 1000 to 12000 centipoise (these viscosities are Brookfield viscosities measured with a viscosimeter in the form of a flat plat rotating at 20 revolutions per minute)

* the gel has a phase difference phi between the controlled shear stress and the resulting shear strain such that $\text{tg}(\phi)$ is less than or equal to 1.5, preferably less than or equal to 1.2. $\text{tg}(\phi)$ is the tangent of the angle phi (or phase difference). The measurement of phi is made by means of a rheometer having a flat fixed plate and a rotating cone above this plate such that the angle between them is less than 10°, preferably less than 4°. The cone is caused to rotate by means of a controlled speed motor; the rotation is a sinusoidal one, i.e., the torque and the angular displacement change as a sine function with time. This angular displacement corresponds to the hereabove mentioned shear strain; the torque of the controlled

SUBSTITUTE SHEET

-9-

speed motor (which causes the angular displacement) corresponds to the hereabove mentioned controlled shear stress

* the gels preferably have a specific gravity greater than 1, preferably greater than 1.05, more preferably greater than 1.1.

* the gels have a spontaneity (as hereafter defined) less than 75, preferably less than 25.

By the expression "continuous system," it is meant a material which is visually homogeneous, that is to say which has the visual appearance of having only one physical phase; this does not exclude the possibility of having small solid particles dispersed therein, provided these particles are small enough not to constitute a visible separate physical phase.

It is known that a gel is generally a colloid in which the dispersed phase has combined with the continuous phase to produce a viscous, jelly-like product; it is also a dispersed system consisting typically of a high molecular weight compound or aggregate of small particles in very close association with a liquid.

By the expression "hazardous product" as used herein is meant a product that may cause damage to the environment or be injurious to a person handling it.

According to one main and preferred feature of the invention, the hazardous product is an active ingredient which is an agrochemical, and more precisely a pesticide or a plant protection agent (including plant growth regulators or plant nutrient).

The invention is not limited to some specific agrochemicals; a list of many agrochemicals which can be used in the invention includes:

- 10 -

Fungicides such as Triadimefon, Tebuconazole, Prochloraz, Triforine, Tridemorph, Propiconazole, Primicarb, Iprodione, Metalazyl, bitertanol, Iprobenfos, Flusilazol, fosetyl, Propyzamide, Chlorothalonil, Dichlone, Mancozeb, Antraquinone, Maneb, Vinclozolin, Fenarimol, Bendiocarb, Captafol, Benalaxyl, Thiram,

Herbicides (or defoliants) such as quizalofop and its derivatives, Acetochlor, Metolachlor, Imazapur And Imazapyr, Glyphosate And Gluphosinate, Butachlor, Acifluorfen, Oxyfluorfen, Butralin, Fluazifop-butyl, Bifenox, Bromoxynil, Ioxynil, Diflufenican, Phenmedipham, Desmedipham, Oxadiazon, Mccopropo, MCPA, MCPB, MCPP, Linuron, Isoproturon, Flamprop And Its Derivatives, Ethofumesate, Diallate, Carbetamide, Alachlor, Metsulfuron, Chlorsulfuron, Chlorpyralid, 2,4-d, Tribufos, Triclopyr, Diclofop-methyl, Sethoxydim, Pendimethalin, Trifluralin, Ametryn, Chloramben, Amitrole, Asulam, Dicamba, Bentazone, Atrazine, Cyanazine, Thiobencarb, Prometryn, 2-(2-chlorobenzyl)-4, 4-dimethyl-1, 2-oxazolidine-3-one, Fluometuron, Napropamide, Paraquat, Bentazole, Molinate, Propachlor, Imazaquin, Metribuzin, Tebuthiuron, Oryzalin,

Insecticides or nematicides such a Ebufos, Carbosulfan, Amitraz, Vamidothion, Ethion, Triazophos, Propoxur, Phosalone, Permethrin, Cypermethrin, Parathion, Methylparathion, Diazinon, Methomyl, Malathion, Lindane, Fenvalerate, Ethoprophos, Endrin, Endosulfan, Dimethoate, Dieldrin, Dicrotophos, Dichlorprop, Dichlorvos, Azinphos And Its Derivatives, Aldrin, Cyfluthrin, Deltamethrin, Disulfoton, Chordimeform, Chlorpyrifos, Carbaryl, Dicofol, Thiodicarb, Propargite, Demeton, Phosalone,

Plant growth regulator such a gibberellic acid, ethyl or ethephon, cycocel, Chlormequat, Ethephon, Mepiquat.

- 11 -

Among those many agrochemicals, the following are of particular interest: the organophosphorus insecticides and the hydroxybenzonitriles herbicides such as bromoxynil or ioxynil either in the form of a salt or an ester.

In order to assess whether a surface-active adjuvant possesses dispersing properties and may be a dispersant according to the invention, the following test is carried out: an aqueous suspension (100ml) containing kaolin or atrazine (50g), in the form of solid particles having a particle size between 1 and 10 microns, and surface-active adjuvant (5g) is left to stand at 20°C for 30 minutes in a graduated cylinder (kaolin is used when the dispersing agent is able to disperse a hydrophilic solid. Atrazine is used when the dispersing agent is able to disperse a hydrophobic solid). After standing, 9/10ths (nine-tenths) of the volume of the suspension, situated in the upper part of the suspension, is removed, without agitation, and the solids content (residue after evaporation of the water) of the remaining tenth is measured; this solids content must not exceed 12% by weight of the solids content of 100 ml of the suspension on which the test is carried out.

The spontaneity is assessed according to the following method: A mixture of 1 ml gel with 99 ml water are put into a 150 ml glass tube which is stoppered and inverted through 180° (upside down). The number of times required to completely disperse the gel is called the spontaneity.

A thickener is a compound which increases the viscosity of a gel or a liquid.

The surfactant that may be used in the invention may be selected from those of the following list (which is non-limitative): salts of lignosulphonic acids, salts of phenyl

-12-

sulphonic or naphthalene sulphonic acids; poly condensates of ethylene oxide with fatty alcohols, fatty acids, fatty esters, or fatty amines, or substituted phenols (particularly alkylphenols or arylphenols); salts of sulphosuccinic acid esters; taurine derivatives (particularly alkyltaurates); phosphoric esters of alcohols or of polycondensates of ethylene oxide with phenols; esters of fatty acids with polyols; and sulphate, sulphonate and phosphate functional derivatives of the above compounds.

The dispersants that may be used in the invention may be selected from those of the following list (which is non-limitative: condensed naphthalene sulfonic acid; polyacrylic acid; sodium sulfosuccinate, calcium lignosulfonate, glycerol stearate, poly condensate of ethylene oxide and propylene oxide.

The present invention also provides a containerisation system (i.e. a container) comprising a water soluble or water dispersible bag containing a gel of the present invention.

The chemical nature of the enveloping film constituting the bags which may contain the composition/gels of the invention can vary quite widely. Suitable materials are water soluble (or possibly water dispersible) materials which are insoluble in the organic solvents used to dissolve or disperse the agrochemical active ingredient. Specific suitable materials include polyethylene oxide, such as polyethylene glycol; starch and modified starch; alkyl and hydroxyalkylcellulose, such as hydroxymethylcellulose, hydroxyethylcellulose, hydroxypropylcellulose; carboxymethylcellulose; polyvinylethers such as poly methyl vinyl ether; poly(2,4-dimethyl-6-triazinylmethylethylene; poly(vinylsulfonic acid); polyanhydrides; low molecular weight urea-formaldehyde resins; low molecular weight melamine-formaldehyde resins; poly(2-hydroxyethyl methacrylate);

- 13 -

polyacrylic acid and its homologs; but preferably the enveloping film comprises or is made from polyvinylalcohol (PVA). PVA is generally partially or fully alcoholysed or hydrolysed, e.g., 40-100%, preferably 80-99% alcoholysed or hydrolysed, polyvinyl acetate film.

Preferred material for constituting the bags for the gels of the invention are polyethylene oxide or methylcellulose, or polyvinylalcohol. When polyvinylalcohol is used, it is advantageously a 40-100%, preferably 80-99% alcoholysed or hydrolysed, polyvinyl acetate film.

The gels of the inventions are generally very easy to make, simply by mixing the components, optionally with grinding or milling.

In order to make a bag, the film must be shaped (possibly partially sealed) and then filled with the gel. Generally the gels are able to flow, even if it is a slow rate due to the high viscosity. A container which is used to contain the gels cannot be easily emptied due to this high gel viscosity (that is a reason why the gels have not been used up to now in agriculture). When filled, the bag must be finally sealed, generally heat sealed, to be closed.

Further information may be found in the following copending applications, the disclosures of which are incorporated herein by reference: application of David Edwards and William McCarthy for "Laminated Bags for Containerization of Toxic or Hazardous Materials" filed April 4, 1991; application of Samuel T. Gouge, Leonard E. Hodakowski, Chi-Yu R. Chen and Paul J. Weber for "Gel Formulations for Hazardous Products" filed April 4, 1991; application of Leonard E. Hodakowski, Chi-Yu R. Chen, Samuel T. Gouge and Paul J. Weber for "Water Dispersible Gel

- 14 -

Formulations" filed April 4, 1991; application of Leonard E. Hodakowski, Ricky W. Couch, Samuel T. Gouge and Robert C. Ligon for "Gel Formulations" filed April 4, 1991; and application of Samuel T. Gouge, David P. Downing, Spencer B. Cohen, Allan J. Luke, Robert D. McLaughlin and James E. Shue for "Bag In A Bag For Containerization of Toxic or Hazardous Material" filed April 4, 1991.

The following examples are given for illustrative purposes and should not be understood as restricting the invention.

In these examples, tg(phi) is less than 1.5

EXAMPLE 1

A gel is made by stirring at 50°C a mixture of:

Active ingredient: 2,4-D phenoxy benzoic acid isooctyl ester):

64.8%

Solvent: aromatic solvent with flash point of 65°C:

23.2%

Surfactant: a mixture of

a non ionic/sulfonate blended emulsifier 4%
and calcium alkylbenzene sulfonate 1%

Gelling agent: mixture of dioctylsulfosuccinate salt
and sodium benzoate

6%

plasticising agent: ethylene glycol 1%.

The mixture is stirred and shaked until each component is dissolved or dispersed.

- 15 -

During stirring, a dissolution appears, and thereafter a gelation. Gelation is increased during the cooling at room temperature (20°C).

The brookfield viscosity of the gel is 3000 centipoise.

The emulsion stability is good in the above described test.

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of the sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 min interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 2

The procedure of example 1 is repeated, except that a mixture containing the following adjuvants is used:

Surfactant: non ionic/sulfonate blended emulsifier:

5.2%

Gelling agent: tetramethyl decyndiol

30%

The brookfield viscosity of the gel is 3000 centipoises.

-16-

The emulsion stability is good in the above described test.

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of this sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 minute interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 3

The procedure of example 1 is repeated, except that a mixture containing the following adjuvants is used:

Surfactant: non ionic/sulfonate blended

emulsifier: 21.5%

and calcium alkylbenzene sulfonate: 3.7%

Gelling agent: ethoxylated dialkyphenol 10%

plasticising agent: a mixture of ethylene glycol

and water at 9 to 1 weight ratio 1%

The brookfield viscosity of the gel is 3500 centipoise.

The emulsion stability is good in the above described test.

- 17 -

1100 g of this gel are put in a 1 liter bag made of film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). the bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 min interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 4

A gel is made by stirring at 50°C a mixture of:

active ingredient:

bromoxynil acid (as the octanoate ester): 30.15%

bromoxynil acid (as the heptanoate ester): 31.15%

Solvent: aromatic solvent with a flash point of 38°C:

21.85%

Surfactant: polyaryl phenolethoxylated 6.0%.

calcium alkylbenzene sulfonate 2.0%

Gelling agent mixture: a clay which has been modified

by addition of methyl groups 6.0%

and propylene carbonate 2.0%

plasticising agent: ethylene glycol 1%

These materials are mixed together while shearing with attritor mixer. The product started to gel in a few minutes.

The brookfield viscosity of the gel is 4200 centipoise.

-18-

The emulsion stability is good in the above described test.

The spontaneity is 38.

1100g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of this sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3min interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 5

The procedure of example 4 is repeated, except that a mixture containing the following components is used:

active ingredient:

bromoxynil acid (octanoate ester): 18.65%

bromoxynil acid (heptanoate ester): 13.85%

methylchloropropionic acid (isooctyl ester): 37.4%

Solvent: Aromatic solvent with a flash point of 38°C: 10.1%

Surfactant: non ionic/sulfonate blender emulsifier: 13%

Gelling agent mixture:

- 19 -

hydrogenated castor oil	3%
ethoxylated vegetable oil	3%
plasticising agent: ethylene glycol	1%

These materials are mixed together while shearing with attritor mixer. The product started to gel in a few minutes.

The brookfield viscosity of the gel is 3150 centipoise.

The emulsion stability is good in the above described test.

The spontaneity is 20.

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of this sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 min interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 6

The procedure of example 5 is repeated except that a mixture containing the following components is used:

active ingredient:

bromoxynil octanoate:	18.4%
bromoxynil heptanoate:	14.0%

-20-
-15-

1.1100 methyl chloropropionic acetic acid (isocetyl acrylate ester): 100 diatomaceous earth are incorporated in the mixture. 36.6%

2. Surfactant mixture: non ionic/sulfonate blended emulsifiers: 2000 OGI is an emulsion of lauryl sulfate and dioctyl ester of sodium sulfosuccinic acid and sodium benzoate: 2.0%

3. Gelling agent: diatomaceous earth: 17.0%

4. Dispersant: sodium sulfonic of naphthalene 3.0%

5. formaldehyde condensate: 1.0%

6. plasticising agent: a mixture of ethylene glycol and water at 9 to 1 weight ratio: 1.0%

These materials are mixed together while shearing with attritor mixture. The product started to have the appearance of a smooth paste, and is a gel in few minutes.

The Brookfield viscosity of the gel is 9000 centipoises.

The emulsion stability is good in the above described test.

The spontaneity is 9.3% over 100 days at 20°C.

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolyzed polyvinyl acetate; cold water soluble; thickness: 0.55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

-21-

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed with a 10 second interval. There is no clogging in the filter which is a 100 mesh screen.

EXAMPLE 7

The procedure of example 1 is repeated, except that a mixture consisting of the following adjuvants is used:

dispersing agent: tetrahydrofuran saturated 12% v/v; the mixture is stirred and when 100% of the component is dissolved, dispersed.

During stirring, a dissolution appears, and thereafter a gelation. Gelation is increased during the cooling at room temperature (22°C).

The Brookfield viscosity of the gel is 300000, which the emulsion stability is good in the above described test.

The dispersion stability is good in the above described test.

1100g of this gel are put in a 1 liter bag made of a film of PVA (85% hydrolysed polyvinyl acetate cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of this sample is also heat sealed and stored at -20°C for 3 days. The bag is then dropped from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump

-22-

recycling). It is dispersed within a 3mm interval. There is no clogging in the filter, which is a 100 mesh screen.

EXAMPLE 8

The procedure of example 1 is repeated, except that a mixture containing the following material is used:

active ingredient

bromoxynil acid (as the octanoate ester): 30.15%

bromoxynil acid (as the heptanoate ester): 31.15%

Solvent: aromatic solvent with a flash point

of 38°C: 23.7%

Surfactant: polyaryl phenolethoxylated 6.0%

calcium alkylbenzene sulfonate 2.0%

Gelling agent: mixture of dioctylsulfosuccinate,

salt and sodium benzoate 6%

plasticising agent: ethylene glycol 1%

The Brookfield viscosity of the gel is 3000 centipoises. The emulsion stability is good in the above described test.

The emulsion stability is good in the above described test:

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full (about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

-23-

Another bag of sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 mn interval. There is no clogging in the filter which is a 100 mesh screen.

EXAMPLE 9

The procedure of example 1 is repeated, except that a mixture containing the following material is used:

active ingredient:

bromoxynil acid (as the octanoate ester): 33.4%

methylchloropropionic acetic acid (isooctyl ester)

35.6%

Solvent: aromatic solvent with a flash point of 38°C:

20.5%

Surfactant: polyaryl phenoxyethoxylated 4.5%

calcium alkylbenzene sulfonate 0.5%

Gelling agent: mixture of dioctylsulfosuccinate salt and sodium benzoate 5%

plasticising agent: ethylene glycol 0.25%

Defoamer: substituted acetylenic diol 0.25%

The brookfield viscosity of the gel is 3000 centipoise.

The emulsion stability is good in the above described test.

1100 g of this gel are put in a 1 liter bag made of a film of PVA (88% hydrolysed polyvinyl acetate; cold water soluble; thickness: 55 microns). The bag, which is almost full

-24-

(about 95% v/v), is heat sealed. The density both of the gel and of the bag containing the gel is 1.1.

The bag is then dropped 10 times from 1.2 m onto the ground. No breaking or leakage is observed.

Another bag of this sample is also made and stored at -20°C for 3 days. The bag is then dropped 5 times from 1.2 m onto the ground. No breaking or leakage is observed.

The bag is put in a tank containing water under gentle agitation (that is to say such as that obtained with pump recycling). It is dispersed within a 3 min interval. There is no clogging in the filter, which is a 100 mesh screen.

- 25 -

CLAIMS

1. A water dispersible organic gel which is a continuous system comprising:

a hazardous product,

5 optionally organic solvent,

a water soluble or water dispersible surfactant,

a gelling agent and

a plasticising agent.

2. A gel according to claim 1 wherein the 10 hazardous product is an agrochemical.

3. A gel according to claim 1 or 2 wherein the hazardous product is a pesticide, a plant protection agent, a plant growth regulator or a plant nutrient.

4. A gel according to claim 1 2 or 3 wherein the 15 gelling agent which is a solid soluble at a concentration of at least 10% by weight in water and at least 10% by weight in a liquid mixture of hazardous product, surfactant and organic solvent, if present, at a temperature above 50°C.

5. A gel according to claim 4 wherein the gelling 20 agent has a particle size less than 40 microns.

6. A gel according to claim 5 wherein the gelling agent has a particle size less than 10 microns.

7. A gel according to any one of the preceding 25 claims wherein the plasticising agent is a compound which is able to reduce the glass transition temperature of polyvinyl alcohol to below room temperature.

8. A gel according to claim 7 wherein the

- 26 -

plasticising agent is a compound which is water soluble or water dispersible and is soluble at a concentration of at least 0.1% by weight in the liquid mixture of hazardous product, the surfactant and organic solvent, if present.

5 9. A gel according to any one of the preceding claims wherein the surfactant is able to form a liquid mixture with the hazardous product in organic solvent, if present, at a temperature above 70°C.

10 10. A gel according to claim 9 wherein the surfactant is able to form a liquid mixture with the hazardous product in organic solvent, if present, at a temperature above 50°C.

11. A gel according to any one of the preceding claims which further comprises one or more of the following:
15 an organic solvent or a mixture of solvents in which the hazardous product is soluble at the concentration in the gel;

a dispersant;
a thickener which is water soluble or water dispersible and which is soluble at a concentration of at least 5% by weight in a liquid mixture of the hazardous product in organic solvent, if present and surfactant; and/or

another additive which is an antifoam agent, a stabiliser, a buffer, or an antifreezing agent.

25 12. A gel according to any one of the preceding claims which comprises by weight:

SUBSTITUTE SHEET

- 27 -

10 to 90% of hazardous product,

1 to 50% of surfactant,

0.1 to 50% of gelling agent,

0 to 80% of solvent;

5 0 to 20% of plasticising agent,

0 to 20% of other additives as defined in claim 11.

13. A gel according to claim 12 which comprises by weight:

25 to 80% hazardous product;

10 2 to 20% of surfactant;

0.5 to 10% of gelling agent;

3 to 50% of solvent;

0.1 to 10% of plasticising agent, and

0.1 to 10% of other additives as defined in claim 15 11.

14. A gel according to any one of the preceding claims which has a viscosity of 500 to 30,000 centipoise.

15. A gel according to claim 14 which has a viscosity of 1000 to 12,000 centipoise.

20 16. A gel according to any one of the preceding claims which has a phase difference (phi) between the controlled shear stress and the resulting shear strain such that tg(phi) is less than or equal to 1.5.

17. A gel according to claim 16 which has a phase 25 difference (phi) between the controlled shear stress and the resulting shear strain such that tg(phi) is less than or equal to 1.2.

- 28 -

18. A gel according to any one of the preceding claims which has a spontaneity less than 75.

19. A gel according to claim 18 which has a spontaneity less than 25.

5 20. A containerisation system comprising a gel as claimed in any one of the preceding claims in a water soluble or water dispersible bag.

21. A containerisation system according to claim 20 wherein the bag comprises a polyethylene oxide; a starch 10 and modified starch; an alkyl or hydroxyalkylcellulose; a carboxyalkylcellulose; a polyvinylether; poly(2,4-dimethyl-6-triazolylethylene); poly(vinylsulfonic acid); a polyanhydride; a low molecular weight urea-formaldehyde resin; a low molecular weight melamine-formaldehyde resin; a 15 polyacrylate, a polymethacrylate or polyacrylic acid or a homologue thereof.

22. A containerisation according to claim 21 in which the bag comprises a polyethylene oxide which is polyethylene glycol; a hydroxyalkyl-cellulose which is 20 hydroxymethyl-, hydroxyethyl- or hydroxypropyl-cellulose; a carboxyalkylcellulose which is carboxy-methylcellulose; a polyvinyl ether which is polymethyl ether; or a polymethacrylate which is poly(2-hydroxyethylmethacrylate).

23. A containerisation system according to claim 21 wherein the bag comprises polyethylene oxide, 25 methylcellulose or polyvinyl alcohol.

24. A containerisation system according to claim

- 29 -

23 wherein the bag comprises polyvinyl alcohol which is 40
to 100% alcoholyzed or hydrolysed polyvinyl acetate.

25. A containerisation system according to claim
24 wherein the polyvinylalcohol is 80 to 99% alcoholyzed or
5 hydrolysed polyvinylacetate.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 91/01352

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)⁶According to International Patent Classification (IPC) or to both National Classification and IPC
Int.C1. 5 A01N25/34 ; A01N25/04 ; B65D65/38

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols	
Int.C1. 5	A01N ;	B65D

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched⁸III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB,A,2 067 407 (FBC) 30 July 1981 see page 1, line 5 see page 1, line 32 - page 1, line 36 see page 2, line 7 - page 2, line 50 see page 3, line 3 - line 4 see examples 2,3 see claims 1,8,9,14,15,23 ---	1-19
Y		20-25
X	PATENT ABSTRACTS OF JAPAN vol. 4, no. 30 (C-2)(512) 15 March 1980 & JP,A,55 004 336 (KIYOURITSU SANITARII K.K.) 12 January 1980 see abstract & WPI, FILE SUPPLIER, Derwent Publications Ltd., London, GB; AN=80-13757C (08) see abstract ---	1-10

⁶ Special categories of cited documents :¹⁰

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 1 28 OCTOBER 1991	Date of Mailing of this International Search Report 07 NOV 1991
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer W. Lamers Lamers

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		Relevant to Claim No.
Category	Citation of Document, with indication, where appropriate, of the relevant passages	
X	<p>WORLD PATENTS INDEX LATEST Section Ch, Week 8739, 25 November 1987 Derwent Publications Ltd., London, GB; Class C, AN 87-274684/39 & JP,A,62 192 301 (KAGAKU E C KOGYO KK) 22 August 1987 see abstract</p> <p>---</p>	1-10, 20, 21, 23
Y	<p>EP,A,0 347 220 (MAY & BAKER) 20 December 1989 see page 2, column 1, line 3 - line 8 see page 2, column 2, line 34 - page 3, column 4, line 33 see page 4, column 5, line 15 - page 4, column 6, line 17 see claims 1,3,4,8,11,13-15,18-22</p> <p>---</p>	20-25
P, X	<p>EP,A,0 420 497 (E.I. DU PONT DE NEMOURS) 3 April 1991 see page 2, line 15 - line 16 see page 2, line 31 - page 3, line 21 see page 4, line 28 - page 5, line 44 see page 7; table 1 see page 10; table 3 see claims 1-21</p> <p>---</p>	1-19
P, X	<p>WO,A,9 105 714 (RHONE-POULENC AGRICULTURE) 2 May 1991 see page 1, line 2 - line 6 see page 1, line 23 - page 2, line 2 see page 2, line 16 - line 21 see page 4, line 16 - line 23 see page 5, line 22 - page 6, line 1 see claims 1,2,4,5,9,13</p> <p>---</p>	20
E	<p>EP,A,0 449 773 (CIBA-GEIGY) 2 October 1991 see page 2, line 1 - line 2 see page 2, line 30 - page 4, line 4 see examples 1-10 see claims 1-3,6-12</p> <p>---</p>	1-10, 14-25
A	<p>US,A,3 892 905 (R.E.ALBERT) 1 July 1975 see column 1, line 12 - line 62 see column 3, line 67 - column 4, line 44 see claim 3</p> <p>---</p>	1-25
A	<p>US,A,3 630 896 (H.OKA ET AL.) 28 December 1971 see column 1, line 16 - line 22 see column 1, line 55 - column 2, line 58 see examples 1,2,7 see claim 1</p> <p>---</p>	1-25
		-/-

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	US,A,3 171 779 (F.C.MCCOY ET AL.) 2 March 1965 see column 1, line 9 - line 12 see column 1, line 57 - column 2, line 3 see column 3, line 26 - column 4, line 29 see column 5, line 4 - line 24 see column 5, line 69 - column 8, line 55 ---	1-25
A	US,A,2 870 058 (D.J.LODER) 20 January 1959 see column 1, line 15 - line 17 see column 1, line 60 - column 2, line 36 see column 3, line 6 - line 13 see column 3, line 38 - line 50 see examples 2-4 ---	1-25
A	RESEARCH DISCLOSURE, no.289, may 1988, pages 281-284, New York, NY, US, see page 281, column 1, paragraph 1 see page 283, column 1, paragraph 3 - column 2, paragraph 3 ---	1-25

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9101352
SA 49212

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 28/10/91

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A-2067407	30-07-81	AU-A- US-A-	6627481 4546108	23-07-81 08-10-85
EP-A-0347220	20-12-89	GB-A- AU-A- AU-A- AU-A- AU-A- EP-A- EP-A- EP-A- EP-A- EP-A- EP-A- EP-A- EP-A- EP-A- EP-A- WO-A- WO-A- WO-A- WO-A- CN-A- GB-A- GB-A- GB-A- GB-A-	2230445 3767689 3837589 3839689 3840389 0347219 0347221 0347222 0420889 0419545 0422060 0422061 8912587 8912588 8912589 8912590 1040550 2222083 2221158 2221159 2221160	24-10-90 12-01-90 12-01-90 12-01-90 12-01-90 20-12-89 20-12-89 20-12-89 10-04-91 03-04-91 17-04-91 17-04-91 28-12-89 28-12-89 28-12-89 28-12-89 21-03-90 28-02-90 31-01-90 31-01-90 31-01-90
EP-A-0420497	03-04-91	AU-A- WO-A-	6432290 9103937	18-04-91 04-04-91
WO-A-9105714	02-05-91	GB-A- AU-A- AU-A- WO-A-	2239443 6631790 6633390 9105715	03-07-91 16-05-91 16-05-91 02-05-91
EP-A-0449773	02-10-91	None		
US-A-3892905	01-07-75	AU-A- BE-A- DE-A- FR-A- GB-A-	3219471 771127 2139112 2104234 1330745	15-02-73 16-12-71 17-02-72 14-04-72 19-09-73

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. EP 9101352
SA 49212

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information. 28/10/91

Page 2

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-3892905		LU-A- 63694 NL-A- 7111068 OA-A- 3777	17-12-71 15-02-72 24-12-71
US-A-3630896	28-12-71	None	
US-A-3171779		None	
US-A-2870058		None	